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Ozone–Water 1:1 Complexes O_3–H_2O: An Ab Initio Study

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Ab initio MO calculations have been carried out for the ozone–water 1:1 complexes in order to elucidate the structures and electronic state of the complexes. The QCISD calculations indicated that three structures are obtained as stable forms of O_3–H_2O. The most stable structure of O_3–H_2O has C_s symmetry where the central oxygen of O_3 and all atoms of H_2O are located on the molecular C_s plane. The dipole of H_2O orients toward the central oxygen atom of O_3 (i.e., dipole orientation form). The other two forms are cis and trans forms of O_3–H_2O where all atoms are located on the molecular plane, and a hydrogen of H_2O binds to one of the terminal oxygen atoms of O_3 by a hydrogen bond. The binding energies of O_3 to H_2O for dipole, cis, and trans forms are calculated to be 2.39, 2.27, and 2.30 kcal/mol, respectively, at the QCISD(T)/6-311++G(3df,3pd)//QCISD/6-311++G((d,p) level. The dipole orientation form is more stable in energy than the cis and trans forms. Rotational constants for the dipole orientation form are calculated to be $A = 11.897$, $B = 4.177$, and $C = 3.318$ GHz which are in good agreement with the experimental values ($A = 11.961$, $B = 4.174$, and $C = 3.265$ GHz). The electronic states of O_3–H_2O were discussed on the basis of theoretical results.

Ozone is one of the reactive species and plays an important role in the upper atmosphere. Therefore, its structure and electronic states have been studied extensively in the gas phase and in the condensed phase, because the chemistry of ozone is important in the depletion of the ozone layer by a series of reactions with atmospheric species. Recently, the importance of the interaction of ozone with atmospheric molecules has been pointed out by several authors.[1−5] The ozone−water complex is one of the key complexes in the reaction of ozone layer.

Microwave spectra of the O_3−H_2O 1:1 complex in gas phase were observed with a pulsed-beam Fabry−Perot cavity Fourier transform microwave spectrometer, giving the rotational constants $A = 11.96058$, $B = 4.17404$, and $C = 3.26517$ GHz.[5] The moment of inertia and dipole moment ($\mu = 1.140$ D) data indicated that the complex has C_s symmetry with water and the unique oxygen of ozone lying in the symmetry plane. This plane bisects the O−O−O angle of ozone. The distance between the center of mass of ozone and water is 2.957 Å.

A few ab initio calculations have been carried out for the O_3−H_2O complexes.[5,6] From the MP2/6-31G(d,p) and MP4SDTQ/6-31G(d,p) calculations, it was found as a candidate of structure of O_3−H_2O that the terminal oxygen atoms of ozone are tilted toward one of the nonequivalent hydrogen atoms in water.[5] The dipole of H_2O orients toward the central oxygen atom of ozone. Later, Zakharrov et al. suggested from the MP4SDQ/4-21G(d,p) calculations that the hydrogen of H_2O orients to one of the terminal oxygen atoms of O_3.[6] Thus, the structure of O_3−H_2O is not clearly understood from a theoretical point of view and is still in controversy.[5,6]

In the present study, high-level ab initio calculations carried out for the O_3−H_2O 1:1 complexes in order to shed light on the structural feature of ozone−molecule complexes in atmosphere. In particular, we focus our attention on the most stable form of the O_3−H_2O complexes whose rotational constants agree with the experimental data.[5] The bonding nature between O_3 and H_2O in the most stable structure of O_3−H_2O is discussed on the basis of theoretical results.

In a previous paper, we investigated theoretically the structures and electronic states of O_3−HF complexes with several conformers.[7] Our ab initio calculations suggested that the structure of O_3−HF has a cis form where all atoms are located on the molecular plane. Also, it was found that the QCISD level of theory needs to obtain a reasonable relative energy for ozone−molecule complexes.

First, the ozone−water complex was fully optimized at several levels of theory. Several conformers were examined as initial geometries of the complex. Finally, three structures,

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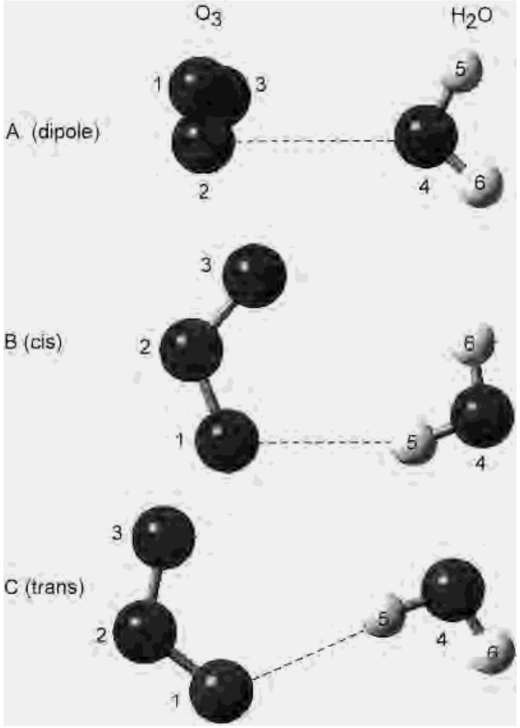

Figure 1. Optimized structure of the ozone−water 1:1 complexes calculated at the QCISD/6-311++G(d,p) level of theory: type A (dipole form), type B (cis form), and type C (trans form).

which are illustrated in Figure 1, were obtained from the QCISD calculations.[8] The first structure (denoted by A type) has C_s symmetry where the H_2O molecule and the central oxygen atom of O_3 are located on the molecular plane. The second and third structures (B and C) are cis and trans forms, respectively, where all atoms are located on the C_s molecular plane in both forms. The structures of the complexes will be discussed using the results obtained by the most sophisticated calculations (QCISD/6-311++G(d,p) level).

The fully optimized parameters are summarized in Table 1. In the optimized structure for A type, the dipole of H_2O orients toward the center oxygen atom of O_3, so that this structure is hereafter denoted by dipole form, also is expressed by A (dipole). The central oxygen atom of O_3 (O2) and all atoms of H_2O (O4, H5, and H6) are located on the C_s molecular plane. The oxygen atoms (O1 and O3) are symmetric each other. The oxygen−oxygen distance between O_3 and H_2O molecules (O2 and O4) was calculated to be $r_{24} = 2.9062$ Å. The terminal oxygen atoms of O_3 (O1 and O3) are slightly tilted toward the water molecule. The structure of O_3 was hardly deformed by the interaction with H_2O: the O−O bond distance of O_3, r_{12}, is calculated to be 1.2540 Å, while the angle O−O−O, ∠OOO, is 117.9° (vs r(O−O) = 1.2555 Å and ∠OOO = 117.8° for free O_3).

For B type, all atoms are located on the molecular plane (C_s plane). The O−O bond distance between O_3 and H_2O was calculated to be $r_{24} = 3.9001$ Å. The H_2O molecule binds to O_3 by a hydrogen bond, and the distance of O1−H5 was $r_{15} = 2.4446$ Å. The hydrogen atom H6 is located in the direction to O_3, so that this structure is cis form.

Table 1. Fully Optimized Geometrical Parameters for the O_3−H_2O Complexes[a]

	MP4SDQ/ 6-311++ G(d,p)	QCISD/ 6-311G(d)	QCISD/ 6-311G(d,p)	QCISD/ 6-311+G(d)	QCISD/ 6-311+ G(d,p)	QCISD/ 6-311++ G(d,p)
			A (Dipole)			
r_{12}	1.2498	1.2542	1.2546	1.2535	1.2540	1.2540
r_{23}	1.2498	1.2542	1.2546	1.2535	1.2540	1.2540
r_{24}	2.9124	2.9363	2.9776	2.8214	2.9153	2.9062
r_{15}	3.4574	2.8432	2.7390	3.4699	3.4607	3.5153
r_{45}	0.9588	0.9575	0.9577	0.9599	0.9591	0.9592
r_{46}	0.9585	0.9568	0.9568	0.9598	0.9587	0.9590
a_{123}	118.1	117.6	117.6	117.8	117.9	117.9
a_{546}	104.0	107.0	103.4	107.2	104.0	104.0
a_{245}	118.8	87.9	80.4	123.0	118.7	121.4
D_{1245}	59.3	61.7	62.4	59.0	59.2	59.1
			B (Cis)			
r_{12}	1.2522	1.2581	1.2581	1.2525	1.2577	1.2577
r_{23}	1.2499	1.2529	1.2530	1.2582	1.2532	1.2532
r_{24}	3.8972	3.8192	3.7438	3.8888	3.9001	3.9001
r_{15}	2.4458	2.3520	2.3479	2.4512	2.4446	2.4446
r_{45}	0.9589	0.9570	0.9570	0.9596	0.9591	0.9591
r_{46}	0.9586	0.9573	0.9571	0.9596	0.9589	0.9589
a_{123}	117.9	117.6	117.74	117.76	117.78	117.78
a_{546}	103.0	106.0	101.9	106.4	103.0	103.0
a_{215}	112.5	106.8	108.0	112.4	112.6	112.6
a_{154}	158.0	172.3	160.5	156.5	158.0	158.0
			C (Trans)			
r_{12}	1.2551	1.2644	1.2636	1.2681	1.2678	1.2678
r_{23}	1.2471	1.2473	1.2480	1.2441	1.2445	1.2445
r_{24}	4.0133	3.9099	3.8971	4.0234	3.8293	3.8293
r_{15}	2.3033	2.3831	2.3822	2.3067	2.3019	2.3019
r_{45}	0.9592	0.9571	0.9574	0.9597	0.9594	0.9594
r_{46}	0.9582	0.9572	0.9572	0.9594	0.9585	0.9585
a_{123}	118.0	117.6	117.6	117.1	117.8	117.6
a_{215}	116.8	104.2	103.5	116.6	116.7	116.7
a_{154}	174.0	163.6	162.3	174.0	174.0	174.0
a_{546}	103.6	106.3	102.5	107.1	103.6	103.6

[a] Bond lengths and angles are in angstroms and in degrees, respectively.

Table 2. Total Energies (in au) Calculated at Several Levels of Theory

	A (dipole)	B (cis)	C (trans)
MP4SDQ/6-311++G(d,p)	3.11	2.00	1.79
QCISD/6-311++G(d,p)	3.07	2.00	1.88
QCISD(T)/6-311++G(d,p)	3.23	2.14	1.98
MP4SDQ/6-311++G(2d,p)	2.61	2.03	1.83
QCISD/6-311++G(2d,p)	2.59	2.03	1.93
QCISD(T)/6-311++G(2d,p)	2.76	2.21	2.05
MP4SDQ/6-311++G(df,pd)	3.18	2.01	1.82
QCISD/6-311++G(df,pd)	3.14	2.00	1.91
QCISD(T)/6-311++G(df,pd)	3.31	2.16	2.01
MP4SDQ/6-311++G(3df,3pd)	2.24	2.04	2.03
QCISD/6-311++G(3df,3pd)	2.23	2.06	2.13
QCISD(T)/6-311++G(3df,3pd)	2.39	2.27	2.30

[a] Geometries are optimized at the QCISD/6-311++G(d,p) level.

C type was also composed of hydrogen bonding between H_2O and O_3 as well as B type, but the hydrogen atom (H6) is located in an opposite position to O_3 (i.e, trans form).

The binding energies of three structural forms are summarized in Table 2.[9] All calculations indicated that type A (dipole) is most stable in energy, and the energy of types B and C (cis and trans forms) are close to each other. Also, the binding energy of type A is largest within three structural forms. The QCISD(T)/6-311++G(d,p)//QCISD/6-311++G(d,p) calculations indicated that the H_2O molecule is bound by 3.23 kcal/mol to the ozone molecule as dipole orientation form (type A). The binding energies for types B and C were calculated to be 2.14 and 1.98 kcal/mol, respectively. The most sophisticated calculations, QCISD(T)/6-311++G-

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(8) See Supporting Information for computational details.

(9) See Supporting Information for total energies.

Table 3. Harmonic Vibrational Frequencies (in cm^{-1}) Calculated at the MP4SDQ/6-311++G(d,p) Level

A (dipole)	B (cis)	C (trans)	O_3	H_2O
a' 4004	a' 3998	a' 3999	a' 1325	a' 4004
a' 3904	a' 3905	a' 3903	a' 1290	a' 3901
a' 1667	a' 1680	a' 1673	a' 767	a' 1656
a'' 1329	a' 1324	a' 1340		
a' 1299	a' 1290	a' 1284		
a' 775	a' 773	a' 773		
a' 322	a'' 388	a'' 323		
a' 264	a'' 336	a' 280		
a'' 162	a'' 284	a'' 194		
a'' 120	a' 258	a'' 162		
a'' 119	a' 81	a' 88		
a' 104	a' 58	a' 25		

Table 4. Rotational Constants (in GHz) Calculated at Several Levels

	A	B	C
A (Dipole)			
MP4SDQ/6-311++G(d,p)	11.961	4.220	3.347
QCISD/6-311G(d)	12.130	4.606	3.566
QCISD/6-311G(d,p)	12.204	4.567	3.536
QCISD/6-311+G(d)	11.895	4.388	3.451
QCISD/6-311+G(d,p)	11.896	4.209	3.338
QCISD/6-311++G(d,p)	11.897	4.177	3.318
exptl	11.961	4.174	3.265
B (Cis)			
MP4SDQ/6-311++G(d,p)	13.404	3.219	2.596
QCISD/6-311G(d)	13.333	3.359	2.683
QCISD/6-311G(d,p)	13.293	3.528	2.788
QCISD/6-311+G(d)	13.309	3.235	2.602
QCISD/6-311+G(d,p)	13.333	3.217	2.592
QCISD/6-311++G(d,p)	13.333	3.217	2.592
C (Trans)			
MP4SDQ/6-311++G(d,p)	14.684	2.882	2.409
QCISD/6-311G(d)	13.681	3.125	2.544
QCISD/6-311G(d,p)	13.640	3.157	2.563
QCISD/6-311+G(d)	14.638	2.867	2.397
QCISD/6-311+G(d,p)	13.640	3.157	2.563
QCISD/6-311++G(d,p)	14.629	2.877	2.404

(3df,3pd)//QCISD/6-311++G(d,p), gave that the binding energies in types A, B, and C are 2.39, 2.27, and 2.30 kcal/mol, respectively. The binding energies of the water dimer are calculated in the range 5.0−7.0 kcal/mol,[10,11] indicating that the hydration energy of O_3 is significantly less than that of the pure water molecule.

The QCISD(T)/6-311++G(d,p)//QCISD/6-311++G(d,p) calculations indicated that type A is 1.09 and 1.25 kcal/mol more stable in energy than types B and C, respectively. The QCISD(T)/6-311++G(3df,3pd)//QCISD/6-311++G(d,p) calculations also gave the similar tendency, although the relative energies are slightly less than those of the calculations (type A is 0.12 and 0.09 kcal/mol more stable in energy than types B and C, respectively).

In order to check stability of the structures obtained by the geometry optimizations, harmonic vibrational frequencies of the complexes were calculated at the MP4SDQ/6-311++G(d,p) level. The results are given in Table 3. All frequencies for three complexes are positive, so that these complexes are located in global minima and are not transition state structures. The higher three modes correspond to those of the H_2O moiety of the complexes, and the next three modes correspond to those of O_3. The vibrational modes of O_3 were slightly perturbed by the interaction with H_2O and were shifted from those of the free molecule. The lower six modes originated from the interaction of O_3 with H_2O. The vibrational frequencies of the H_2O moiety in A type were close to those of free H_2O, whereas the O−H stretching modes of H_2O moiety in O_3-H_2O (cis and trans forms) were red-shifted from free H_2O.

Table 5. Charges on Each Atom of the O_3-H_2O Complexes, Free O_3, and Free H_2O Calculated at the QCISD/6-311++G(d,p) Level

atom			A (dipole)	B (cis)	C (trans)	free O_3	free H_2O
O_3	1	O	−0.20	−0.17	−0.15	−0.13	
	2	O	+0.44	+0.29	+0.23	+0.26	
	3	O	−0.20	−0.13	−0.06	−0.13	
H_2O	4	O	−0.56	−0.50	−0.51		−0.48
	5	H	+0.25	+0.26	+0.25		+0.24
	6	H	+0.27	+0.24	+0.24		+0.24

Rotational constants of the complexes were calculated at several levels of theory. The results are listed in Table 4. For A type, the rotational constants were calculated to be $A = 11.897$, $B = 4.177$, and $C = 3.318$ GHz, which are in excellent agreement with the experimental values ($A = 11.960584$, $B = 4.174036$, and $C = 3.265173$ GHz). On the other hand, rotational constants for types B (cis) and C (trans) were in poor agreement. These results indicated strongly that ttype A (dipole form) is a strong candidate for the structure of O_3-H_2O observed experimentally in gas phase.[5]

In order to elucidate the bonding nature of H_2O to O_3, the electronic states were analyzed in terms of charges on each atom. The atomic charges of the complexes, free O_3, and free H_2O are given in Table 5. In the free O_3 molecule, the central oxygen atom has a positive charge (+0.26), whereas the terminal oxygen atom has a negative one (−0.13). In types B and C, the charges on the central oxygen atoms are calculated to be +0.29 and +0.23, indicating that the charges on the central oxygen atoms are slightly perturbed by the interaction with H_2O, but the differences are negligibly small. On the other hand, in type A, the charge on the central oxygen atom is enhanced to be +0.44 by the interaction, which is significantly larger than that of free O_3 (+0.26). This indicates that the dipole of the water molecule in type A induces the intermolecular charge separation of O_3. This feature is important in the strong interaction for type A. Also, the charges on the H_2O molecules in types A, B, and C are −0.04, 0.0, and −0.02, respectively, indicating that a large amount of electron density is transferred from O_3 to H_2O in type A. Therefore, the positively charged oxygen atoms (namely, the central oxygen atom of O_3) interact strongly with the negatively charged oxygen atom (namely, water oxygen) in type A. This is the origin of the dipole form of the complex (type A) showing a large binding energy.

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Supporting Information Available: Additional computational details and additional table. This material is available free of charge via the Internet at http://pubs.acs.org.

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